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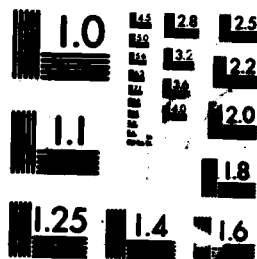
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CRITICAL REVIEW OF CEMENT
-BASED STABILISATION/SOLIDIFICATION
TECHNIQUES FOR THE DISPOSAL
OF HAZARDOUS WASTES

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SUMMARY

The materials used in stabilisation/solidification processes (OPC, PFA and sodium silicate) have been reviewed in terms of their basic composition and chemistry. The addition of inorganic wastes to OPC and PFA has been demonstrated to affect early hydration and has led to the development of the protective coating theory and sorption of heavy metals by PFA as the principal factors involved in stabilization. The aqueous chemistry of OPC, PFA, PFA/OPC and PFA/OPC/SILICATES has also been reviewed and has illustrated the chemical reactions taking place during the first hour of the stabilisation process. Methods to improve the efficiency of the Sealosafe process have been highlighted particularly with respect to supernatant formation. New developments such as the use of clays have been highlighted.



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1.0 INTRODUCTION

Interest in the use of cement-based stabilisation/solidification processes around the world is increasing at the present time. Much of this interest is centered in the States where increasing stringency of legislation, particularly the Resource and Recovery Act (RCRA), is likely to reduce dramatically the landfill disposal option and promote some form of pre-treatment requirement, ie stabilisation/solidification.

Within the UK, the stabilisation/solidification option is handicapped by the low cost of conventional landfill of hazardous material. In addition, some scepticism has arisen concerning the efficiency of the processes particularly as regards the stabilisation/solidification of organic wastes.

Nevertheless, the interest in these processes has been sufficient to promote research programs by various groups around the world. These groups include:

- (1) The United States Environmental Protection Agency
- (2) Environment Canada
- (3) Alberta Environment Centre
- (4) Louisiana State University (LSU)
- (5) Imperial College (IC)

The first three are primarily interested in the regulatory aspects ie testing methods to evaluate potential long-term behaviour of stabilised/solidified products. For instance, the particular interest of the Alberta Environment Canada is to assess the effects of extremes of temperature, common to Alberta, on the structural properties of the final product.

LSU and IC have adopted similar approaches to each other which has been to study the fundamental mechanisms of stabilisation by means of correlation of certain micro and macro properties of the stabilised wastes.

1.1 OBJECTIVES

The objectives of this study are therefore:

- (1) To review critically the use, to date of cement-based stabilisation techniques in the UK and N. America;
- (2) To comment on recent research on these processes;
- (3) To predict future developments in the use of these techniques; and
- (4) To suggest future research needs.

2.0 MATERIALS

Much of the research carried out has involved the use of either Chemfix or Sealosafe. These two processes will be discussed in detail as the fundamental mechanisms are common to all fixation systems which utilise cement or pozzolanic material.

Cement based fixation systems are the most commonly employed stabilisation/solidification techniques because of the relatively low capital and running costs and the relatively simple processing technique when compared with organic encapsulation systems.

Chemfix and Sealosafe are both cement-based stabilisation/solidification processes which have been operated in the UK and the US for the disposal of toxic waste. British patents No 1, 337, 301 and 1,418,215 describe the Chemfix processes. Basically, Chemfix is an inorganic process based on an Ordinary Portland Cement (OPC) and sodium silicate formulation. The stabilisation/solidification process involves mixing a predetermined amount of cement with a contaminated liquid followed by the addition of the settling agent, sodium silicate. The resulting slurry is transferred or pumped to a nearby lagoon to set and cure. The reagent levels added are

related to the required strengths of the final solid - either soft and clay-like or hard and rock-like. The process is claimed (1) to be based on three phases of reaction: an initial rapid reaction between the soluble silicate and all polyvalent metal ions to form insoluble metal silicates, followed by a slower reaction between the silicate and reagent to form a gel, and lastly the hydration of cement. The final product is thought to be built on tetrahedrally co-ordinated silicon atoms alternating with oxygen atoms along the backbone of a linear chain (1). The pollutant metal ions are ionic bonded between adjacent chains to form a cross-linked, three-dimensional, polymer matrix similar to the pyroxene mineral.

The Chemfix process has been operated using a mobile plant on individual sites. Sealosafe, on the other hand is a process based on cement and pulverised fuel ash (PFA) and is described in British patent No 1,485,625. This process involves the stepwise addition of predetermined quantities of cement and PFA to the slurried waste. The slurry is then discharged and/or transported to a lagoon to set and cure. The final product is claimed to be leach free with a rock-like feature. The mechanism of such a stabilisation/solidification process is claimed (2) to be based on 'crystal capture' which is a combination of two interdependent reaction mechanisms: pollutants present in pollution form as ions and react with the OPC/PFA forming strong bonds and the pollutants present in insoluble form are dispersed and trapped within a polymer matrix (Figure 1).

Three solidification plants are in operation in the UK. The process is said to be divided into five unit stages. These are: (2)

- (1) Reception;
- (2) Disintegration, during which the waste is dispersed into a suitable form for treatment;
- (3) Pretreatment to convert certain wastes into a chemical form suitable for stabilisation (eg. for arsenic, chromium and cyanide wastes);
- (4) Stabilisation: Mixing of stabilisation agent with waste to form a slurry;
- (5) Disposal: Slurry is transported away to land disposal site to set and cure.

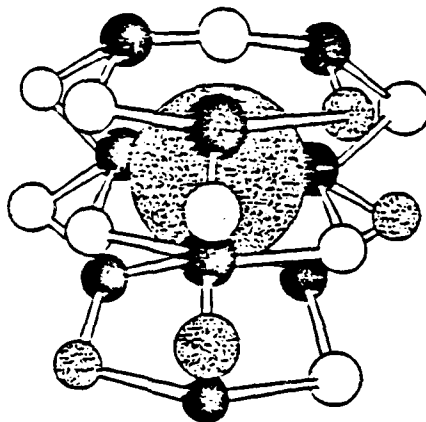


Figure 1 The crystal Capture mechanism
claimed for Sealosafe.

Most solidification/stabilisation systems currently marketed do not approach the problem of the fundamental chemistry of the waste and stabilising agents, but depend primarily on the isolation of the potentially harmful wastes in a coherent block of material to minimise leaching by physical means. For cementitious systems, leaching can be reduced by any process that accelerates the curing and/or limits the porosity of the solidified product (eg. by using an extreme low water/cement ratio or the use of polymer impregnation techniques). It has also been demonstrated in radioactive waste research that wastes cast at elevated temperature and pressure possess leaching characteristics which are similar to the borosilicate glass process.

However, the fundamental chemical reactions and mechanisms of the cement based process as applied to hazardous waste have not been thoroughly studied by the vendor companies before marketing and the process designs are mainly based on an empirical approach using trial-and-error methods of proportioning waste to reagent level. Although there are some published data on the leaching and physical properties of the solidified product, scientific interpretation of these data is not possible because many of these results are based on non-standard testing methods with no mention of reagent level and curing regime used (3). A good summary of these results can be found in reports published by the United States Environmental Protection Agency, giving some leaching, physical properties, compatibility and cost comparison data of these processes (4-6).

2.1 BASIC COMPOSITION OF ORDINARY PORTLAND CEMENT (OPC) AND PULVERISED FUEL ASH (FA)

The main constituents of anhydrous OPC are tricalcium silicate (C_3S about 50% by mass), dicalcium silicate (C_2S ca. 25%), tricalcium aluminate (C_3A ca. 10%) and an aluminoferrite phase approximately to the formula C_4AF (ca. 10%) (7). The hydration chemistry is dominated by the calcium silicate phases and these provide the main sources of strength development in the cement paste. Other minor constituents include free lime and gypsum: the latter is added as a setting agent.

Table 1 Oxide content (%) of ordinary portland cement and pulverised fuel
ash

	OPC	PFA
SiO ₂	20.1	47.1
Al ₂ O ₃	5.3	29.8
Fe ₂ O ₃	3.5	11.6
CaO	64.6	2.3
MgO	1.3	1.6
SO ₃	2.8	0.7
Na ₂ O	0.13	1.3
K ₂ O	0.77	3.6
LOI	0.8	4.4

Pulverised fuel ash, on the other hand is a pozzolanic material, possessing no cementitious properties of its own but able to react with the lime liberated during the hydration of calcium silicate in cement to produce calcium silicate hydrates (C-S-H). Glassy particles in PFA are responsible for most of the chemical reaction. The quantity is probably closely related to the sum of (SiO₂ + Al₂O₃ + Fe₂O₂) in the ash (8). X-ray diffraction analysis has identified some crystalline phases, mainly quartz, mullite, hematite and magnetite. It has been suggested that as far as the pozzolanic reaction is concerned, the mineralogical composition of PFA is more important than its chemical composition (9). Unburnt carbon may constitute a few percent of the ash which is accounted for by the loss of ignition (LOI). The PFA largely comprises insoluble compounds with less than 2% (W/W) of readily soluble material (10). Most PFA has a thin layer of acid sulphate surrounding an alkaline core that contains some free lime. Most soluble matter would finally appear in water as sodium, potassium and calcium sulphate.

It should be noted that the characteristics of PFA vary with its source. Even from a single source, these characteristics may be quite variable, depending on factors such as the source of coal, degree of pulverisation, age of plant, operating conditions and PFA collection and processing method (8).

2.2 BASIC CHEMISTRY OF OPC

When OPC is allowed to mix with water, chemical reactions occur. Generally, the aqueous environment of an OPC/water system becomes very alkaline, with a pH-12.5, after the initial mixing (11). Calcium and SO_4^{2-} concentrations rise gradually, resulting from the dissolution of cement, mainly due to the presence of lime and gypsum. Concentrations of silica and alumina are much lower than that of Ca, this effect is generally accounted for by the 'induction mechanism'.

These reactions are accompanied by the liberation of heat and the hydration reaction can be followed by calorimetric methods (12). A typical exotherm is presented in Figure 2.

The hydration reaction occurs in a number of distinct stages. These are characterised by an initial evolution of heat with a later more gradual peak reaching a maximum after about 8-10 hours, decreasing slowly thereafter. The peaks are separated by an 'induction period' when the rate of heat evolution drops to a very low value (13). The reasons for such a dormant period are not clear but there are various explanations including the formation of a gelatinous product of hydration forming a coating around the cement grain, or delayed nucleation of Ca(OH)_2 crystals affecting the chemical equilibrium for hydration (12).

All four major phases in OPC react with water to form hydration products. These four phases do not react independently and there is a complex interaction between each phase (Figure 3).

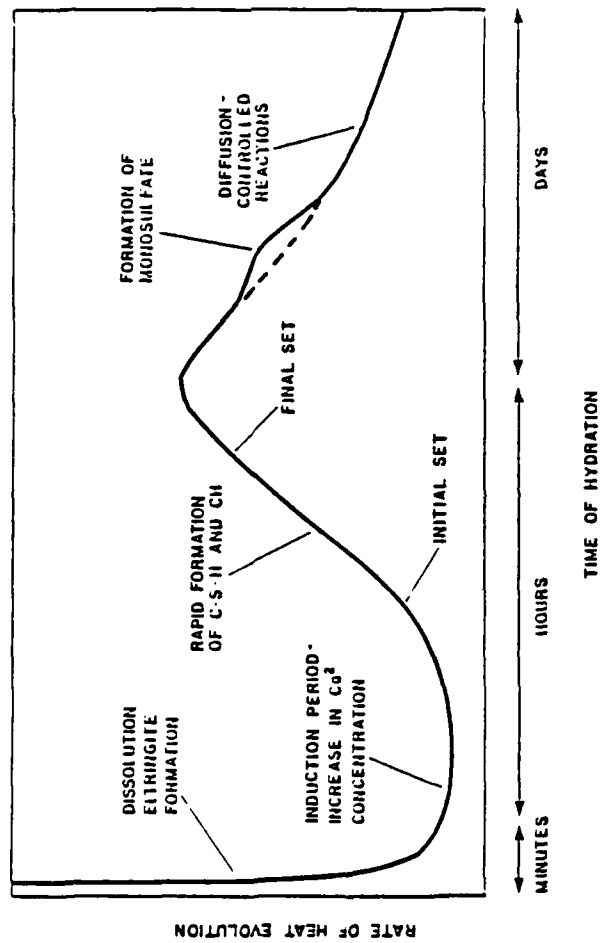


Figure 2 Typical esotherm of hydrating cement paste

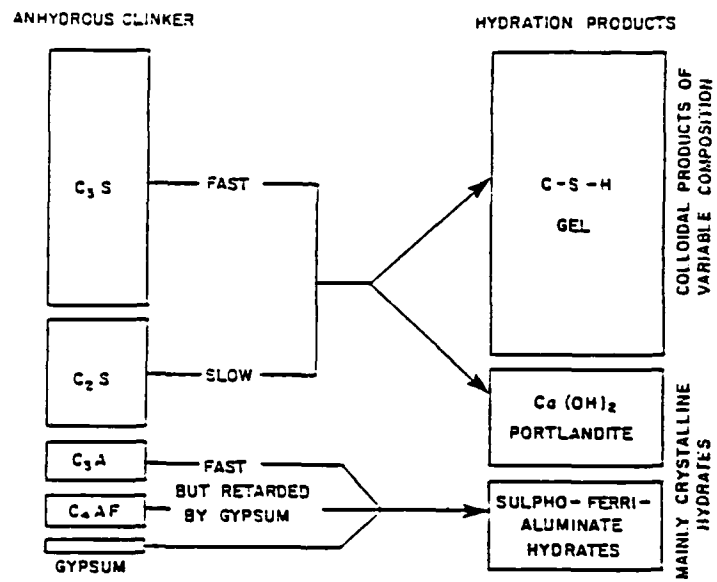


Figure 3 Schematic showing hydration reactions of Portland Cement

2.3 BASIC CHEMISTRY OF PFA/OPC SYSTEMS

The solution chemistry of PFA/water system is different from that of OPC. When water is first added to the anhydrous PFA, the more acid layer dissolves first and the water becomes temporarily slightly acidic (10). The alkaline core then reacts with the other material in the water becoming alkaline. Typical concentrations of the main parameters are presented in Figure 4. The exact nature of the curve, the time taken to react neutrality and the final pH depends on the source and particle size of the PFA and on the water/PFA ratio. PFA is a pozzolanic material and does not possess a cementitious/hydraulic ability. Cabrera and Plowman (14) identified three mechanisms by which PFA interacts with OPC in the blended cement system.

- (i) A physical effect: lubrication of the mix by mainly spherical PFA particles allows the water demand of the mix to be reduced, with no loss of workability.
- (ii) A rapid chemical reaction: soluble ions from PFA react with the calcium aluminates in the cement and retard their hydration.
- (iii) A longer term pozzolanic reaction: silica and alumina from the PFA react with calcium hydroxide produced by the hydration of the calcium silicates in the cement.

The first two reactions are important in the first phase of the reaction, affecting the workability and settling of the blended cement. The third pozzolanic reaction, is the major reaction as far as stabilisation is concerned.

The amorphous particles in PFA are probably the most important pozzolanic constituents partaking in the pozzolanic reaction. Some of the possible reactions are: (14).



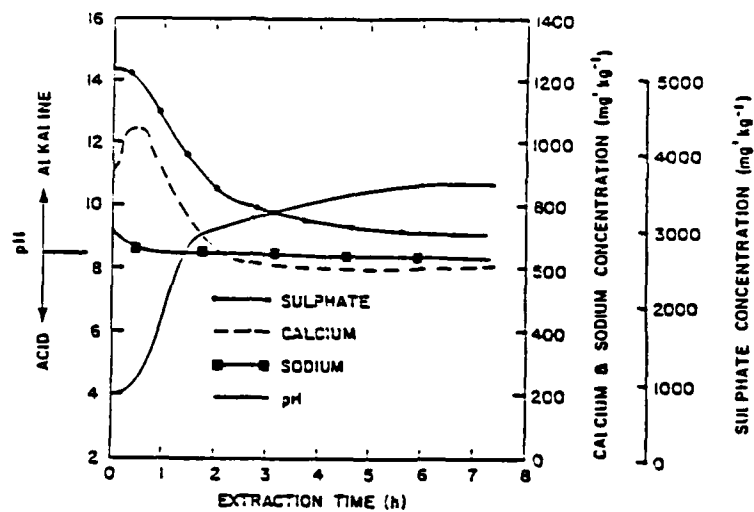


Figure 4 Initial aqueous environment of PFA/Water system

At normal temperatures the lime-pozzolanic reaction is slow (15), the rate of reaction being dependent on the reactivity of the glassy materials present. This in turn depends on the surface area and degree of amorphousness of the material. PFA has a relatively low surface area ($\sim 1 \text{ m}^2 \text{ g}^{-1}$) (15). Although lime from the hydration of OPC is available soon after the addition of water, it is due to the low surface area of the PFA that the pozzolanic reaction is not significant until several weeks hydration have taken place.

For most structural applications the pozzolanic content of a PFA/OPC blended cement is limited to 20 - 25 per cent (15). This is because of the required early strength; for instance at stages 3 and 7 days, it is generally reduced in direct proportion to the amount of pozzolana present in the cement. Another disadvantage of blended cement is the prolonged moist curing needed for the pozzolanic reaction without which the potential benefits of high ultimate strength and superior chemical durability cannot be realised.

2.4 BASIC CHEMISTRY OF SODIUM SILICATE

Soluble silicates have been used as additives in the stabilisation/solidification process (eg. in Chemfix); the most widely used silicate is aqueous sodium silicate. The various types of sodium silicate normally marketed are listed in Table 2.

Sodium silicate solution is alkaline in nature: the pH value of the available silicates lies in the range of about 11 to 13 (16). The solution is strongly buffered by soluble silica in solution. Hence, within limits, the silicate solutions will maintain a fairly constant pH despite the additions of acid and the high pH of the solutions is maintained as acids are added until the alkali is almost neutralised.

Table 2 Types of sodium silicate

SiO_2 : Na_2O	NAME	FORMULA
1 : 2	Sodium orthosilicate	Na_4SiO_4
2 : 3	Sodium sesquisilicate	$\text{Na}_6\text{Si}_2\text{O}_7$
1 : 1	Sodium metasilicate	Na_2SiO_3
2 : 1	Sodium disilicate	$\text{Na}_2\text{Si}_2\text{O}_5$

Several classes of materials react with sodium silicate to form sols or gels. These materials include acids, acid forming materials such as chloride and bicarbonates, some organics and most importantly, as far as stabilisation processes are concerned, salts of heavy metals such as calcium, copper and lead.

When a polyvalent metal salt is mixed with a sodium silicate solution two specific reactions will take place. First, the insoluble metal silicate will be precipitated and second, the increase in pH in the environment of the metal ion at some point causes the formation of a colloidal metal hydroxide. This may be visualised as an absorption of metal ions on gelatinous silica during mutual coagulation of the positively charged colloidal metal hydroxide and negatively charged colloidal silica (17). This suggests that no definite compounds are formed and that the hydroxides are precipitated along with the insoluble metal silicate.

Structurally, the precipitated gel of hydroxide and silicate is essentially amorphous in nature. In soluble silicate, the silicate ions are polymerised to form a mixture of polysilicate ions of non-uniform size. Upon precipitation, they cannot arrange themselves along with metal ions into a regular crystal lattice. The mutual coagulation of silicate and hydroxide further inhibits the formation of regular crystal structure and therefore the insoluble precipitate is always amorphous.

Such a precipitate consists of three-dimensional network made up of a chain of particles that may range in size from polysilic acid units each containing only a few silicon atoms, to colloidal silica particles containing thousands of silicon atoms. The particles are bonded together into chains, probably by hydrogen bonding. However, with the surface SiOH group the Si-O-Si bond could be formed when these particles come together upon consolidation (16).

Thus it can be concluded that such a gel formed between polyvalent ions and soluble silicate has a very unstable mix composition. The properties of such a gel, i.e. strength, durability and permeability, may vary greatly depending on factors such as the concentration of the solution, $\text{Na}_2\text{O}:\text{SiO}_2$ ratio, temperature and the kind of salt with which it reacts (16). Frequently, these gels have a high specific surface area and are capable of acting as selective absorbents. On ageing the gel shrinks, becomes opalescent, cracks and dissolves readily in caustic solution. Shrinkage is the most important process leading to the deterioration of gel. Shrinkage may be caused by syneresis (ie. spontaneous expulsion or erosion by groundwater). Thus the life of such a gel is limited, especially when it is exposed to air or basic groundwater.

3.0 MECHANISMS OF IMMOBILISATION OF HEAVY METALS IN CEMENTITIOUS MATRICES

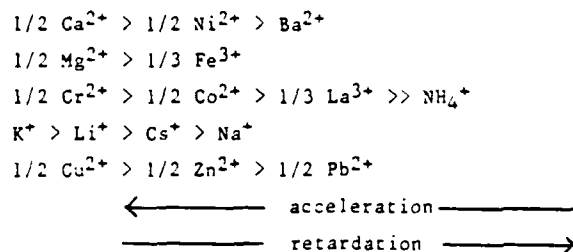
3.1 MODIFICATION OF EARLY HYDRATION OF OPC

In the cement industry inorganic cations have been used as admixtures to facilitate mix design (18). The chemical and physical effects of metal electrolytes on cement or clinker hydration have been studied and are useful in evaluating the interaction between heavy metals and stabilising agents in the cement-based stabilisation/solidification processes.

The effect of adding metal electrolytes have been studied using conduction calorimetry (19). The influence of any electrolyte on the early hydration and heat evolution of cement is threefold:

- (1) The length of time of the induction period;
- (2) The time of maximum rate of heat evolution, and
- (3) The total heat evolution.

In general, an accelerator shortens the induction period and produces an early heat peak with a corresponding increase in height of the maximum rate of heat evolution. A retarder has the reverse effect. A ranking sequence of cations based on this calorimeter method has been compiled by Wilding *et al.* (21).



Also based on this calorimetric method Kando *et al.* (20) suggested that, generally, salts forming the least soluble hydroxides have the greatest retarding effect, while salts forming hydroxides of high solubility exhibit only a slight degree of retardation. The alkali metals capable of forming soluble hydroxides, act as accelerators.

These studies demonstrate that the early hydration reactions of cement are modified by the incorporation of heavy metals. This has an important implication on the mechanism of immobilisation of heavy metals by cement-based stabilisation/solidification processes.

3.2 PROTECTIVE COATING THEORY

Micro-structural studies using scanning electron microscopy (SEM), X-ray diffraction (XRD) and mercury porosimetry have been used to identify the reactions and mechanisms taking place when metal solution is mixed with cement. In a study into the effect of $\text{Pb}(\text{NO}_3)_2$ on the early hydration of Portland cement, Pb was rapidly precipitated from the aqueous solution. Furthermore it was demonstrated that the precipitation was largely in a colloidal gelatinous form coating the surface of the cement grain. The composition of the coating was not simply a $\text{Pb}(\text{OH})_2$ - as would be expected from an alkaline environment - but was a mixed basic Pb salt of variable stoichiometry, involving both nitrate and sulphate. It was postulated that this kind of colloidal membrane formation was typical of precipitation processes that occur within a narrow zone between two solutions with high degree of supersaturation. It was further suggested that similar reactions would take place for cations with similar properties (*viz.* Cu, Zn, Sn, Cd). This coating did not completely stop the hydration of cement and water was able to diffuse through the membrane and be in contact with the cement. Therefore, the extent of retardation of different metals on the hydration depends not only on the fine structure of the coating but also on its chemical composition. Any changes in the structure of the coating (chemical conversion or crystallisation) could render it less effective and initiate further hydration of the cement.

Based on this study and some previous findings (23,24) it was suggested that cement hydration was normally self-inhibiting and the cement hydration largely controlled by diffusion through the protective colloidal coating around the cement grain (25).

Therefore the rate of reaction and the associated hydrate development will depend on the permeability and cohesion of the coatings. The additions of additives or admixtures would modify this coating to either a more open flocculated structure accelerating hydration or a dense coagulated layer resulting in retardation (Figure 5).

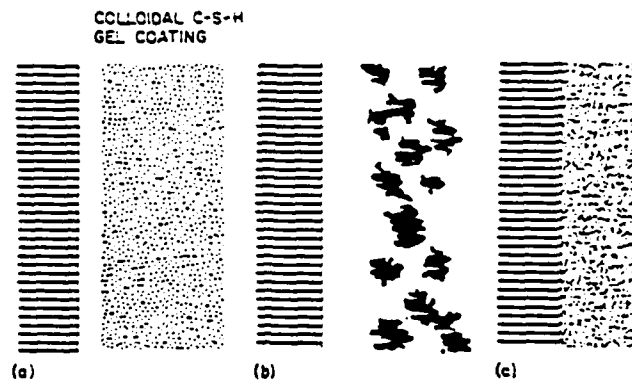


Figure 5 Schematic representation of possible changes in the colloidal structure of a C-S-H gel coating on a cement grain surface. (a) Normal protective gel coating, inhibiting hydration. (b) Floculated, poorly adherent coating permitting accelerated hydration. (c) Dense, coagulated and strongly adherent coating causing retardation of hydration.

Corroborative evidence of the protective coating theory was provided by Stepanova *et al.* (26) for Cu and Zn cations. They attributed this coating to a complex formation between the additives and the components of cement giving a complex whose stability made a substantial contribution to the compressible strength of cement. They ranked the effectiveness of these additives in affecting the strength of cement in the sequence $Mn < Co < Ni > Cu > Zn$. This ranking corresponds to the variation of the enthalpies of complex formation and of the stability constants of complexes of the given metals with various ligands.

Separate studies have been concluded to investigate the effect of solid metal oxides and hydroxides on the hydration of individual clinker component of cement using differential calorimetry, SEM and XRD. Tashiro and co-workers (27,28) concluded that Cr_2O_3 , $Cu(OH)_2$ and ZnO retarded the hydration of C_3A through the formation of cubic calcium aluminate hydrate. Lead oxide, however, only retarded the initial reaction and then accelerated the hydration after a few minutes. On adding gypsum on the C_3A system, the same authors found that the addition of these metal oxides and hydroxides promoted the crystal growth of ettringite (calcium aluminate sulphate hydrate) and produced a significant change in the micro-structure hence affecting the physical strength of the hydrated paste. Therefore an additional effect of adding heavy metals to the cementitious matrices is to promote the formation of calcium sulphasaluminate hydrates (29). The increased production of crystalline monosulphate phases, AFt and AFm , expanded the pore structure and resulted in an increase in total pore volume. This has an important implication on the physical properties of cement.

3.3 SORPTION OF HEAVY METALS BY PFA

The possible use of pulverised fuel ash (PFA) to retain heavy metals has been studied by a few workers. Pandat *et al.* (33) found that PFA was able to remove Cr(VI) from solution. The maximum removal was observed at pH 2. It was suggested that absorption was first governed by diffusion followed by surface compound formation. The adsorption of anions, however, decreased as the pH of the solution increased. Papachristou (34) studied the retention of Pb by PFA and attributed the relation partly to chemical reactions between Pb ions or ions of other heavy metals and the CaO, Al₂O₃, SiO₂, MgO, CaSO₄ present in PFA.

The retention of fluoride by PFA has also been demonstrated by Tasitouridou *et al.* (35). The mechanism was found to be due to the adsorption and chemisorption of fluoride by active alumina in the PFA which causes a positive change in the acidic environment. The above studies show that PFA is able to act as sorbent for heavy metals in the cement based stabilisation/solidification process.

Bishop *et al.* (36) have studied the leach rate of heavy metals from a solidified cementitious waste product using OPC as a solidifying agent. Using two particle sizes for the leaching experiment. They found that the leach rate was lower for smaller particles (contrary to general belief that higher leach rates are associated with high specific surface areas). They postulated that heavy metals are bound to the particles by a sorption mechanism: the increased surface areas of the smaller particles would cause greater ion exchange and adsorption of heavy metals and thus lower leach rates. The results also demonstrated that Cd leached more easily than Cr and Pb which was attributed to the alkaline environment of cement hydration precipitating the insoluble cadmium hydroxide thus reducing reactions with the silicate component of hydrating cement. Chromium and lead, on the other hand, were able to form anionic species in the highly alkaline environment and were involved in the reaction with silicates and aluminates. They suggested also that cadmium was primarily bound to the solid cementitious matrix by a surface-related mechanism (such as ion exchange and adsorption) which chromium and lead were bound into the silicate matrix of the hydrating cement paste.

Such interpretation was not substantiated by any microscopic or crystallographic data. The authors found that the alkalinity of cement was the main cause for metal immobilization. Once the leached alkalinity/added acid ratio fell below 1, then an increase in leached metal concentrations occurred. However, a substantial amount of the heavy metals was found to remain within the solidified waste after all the alkalinity had been neutralized indicating that mechanisms other than simple hydroxide precipitation were involved in immobilisation. The leach rate of the anionic arsenide waste was high indicating that the cement based process was incapable of immobilizing anionic wastes.

3.4 AQUEOUS CHEMISTRY OF OPC, PFA AND PFA/OPC AND PFA/OPC SILICATES

An important factor governing the physical and chemical stabilisation of waste is the initial chemical environment pertaining when the processing agents and hazardous materials are mixed in water. Similar work of this nature has been performed by Environment Canada and Imperial College. The latter work utilised OPC and PFA in water-and-metal solutions in the ratio of liquid/solid = 5 under an inert (nitrogen) atmosphere. The mixes were mixed constantly and samples periodically extracted from the slurry and filtered prior to analysis. These experiments provided an understanding of the initial (ie. within the first hour) chemical reactions involved in stabilisation/solidification.

The most important conclusion drawn from the study is that while the hydration of OPC results in an alkaline aqueous solution, PFA results in a neutral or slightly acidic solution. The replacement of PFA by OPC increases the alkalinity of the aqueous PFA/OPC environment. Accompanying the liberation of lime from the systems is the dissolution of the anhydrous clinker phase of cement releasing calcium. The implication of these findings is that the alkaline environment of the OPC and PFA/OPC systems would render insoluble many of the polyvalent metal ions (eg. Zn and Cd) in the early minutes of the reaction. The concentrations of Cd - which forms hydroxides of very low solubility - dropped to a very low level immediately after mixing. A similar study on Pb by Thomas *et al.* (22) corroborates this results. Zinc, which forms a precipitate with the hydroxyl ion but possesses an amphoteric nature, also decreased rapidly to a low value but the

concentration was slightly higher than those for Cd. A point to note is that the PFA/OPC system can immobilize more Zn than the pure OPC system. This was due to the PFA providing a buffer which lowers the pH, preventing the resolubilisation of Zn.

For metals which do not form insoluble hydroxides (eg. Hg and Cs) the exact concentration profile depends on the specific chemical reaction between the metal and OPC or PFA. Cement has been shown to be incapable of immobilising Cs (32), due to the strong positive charge of the Cs^+ ion, but PFA has been demonstrated to be able to adsorb Cs. Mercury, on the other hand undergoes a moderate progressive decrease in concentration in the OPC and PFA/OPC systems probably due to the precipitation of the HgO and adsorption onto the PFA particles (37).

However, it has been pointed out (33) that the sorptive properties of the PFA particles would be effectively reduced with time once cement is introduced into the system due to (i) the reaction of the PFA with Ca(OH)_2 leading to a decrease in the amount of both and (ii) possible competition for the 'active' sites responsible for both the uptake of heavy metals in the waste and the alkali metals in the cement pore fluids.

Because of the variable nature of both the composition and mineralogy of PFA, it is difficult to generalise the mechanisms of the reaction between heavy metals and PFA or PFA/OPC blended systems. However, for typical British flyash which has a low lime content, the results of a study by Imperial College indicate that PFA possess little retention potential for Zn, Cd and HgCl_2 in the early hours of the reaction. This is due to the low lime content of the PFA and its inability to form hydroxyl compounds rendering the heavy metals insoluble. Microscopic evidence based on SEM confirmed there were no precipitation or gel formations on the PFA particles. Mercuric nitrate, however, was retained which is thought to be due to cation exchange in the slightly acidic medium.

3.5 CORRELATION OF MICRO AND MACRO PROPERTIES OF STABILISED/SOLIDIFIED HAZARDOUS WASTES

It has been suggested that when heavy metals are added to cement, a protective coating will be formed around the cement particles. This coating inhibits further hydration of the cement grain. The protective coating theory was examined by means of a unique extended x-ray absorption fine structure (EXAFS) study conducted by Imperial College at the Daresbury Synchrotron facility. This technique measures the variation of adsorption of x-ray photon energies at energies above the adsorption edge of an atom. When an atom is bombarded by monochromated x-ray radiation, an abrupt increase in the adsorption energy occurs corresponding to the energy level at a particular atom. For atoms embedded in a condensed phase, a sinusoidal variation of the x-ray adsorption as a function of photon energy is observed. This spectra, known as an EXAFS, after suitable analysis, can provide structural information on the local environment in amorphous solids such as cements, glasses and stabilised inorganic wastes.

The EXAFS study on Zn supported the protective coating theory by identifying a clearly defined 4 co-ordinated oxygen shell around the Zn atom in zinc-dosed stabilised waste. Although the local environment beyond this first shell could not be identified it was postulated that the second shell consisted of a mixture of O-H and Si atoms. This was in accord with the results of Bishop *et al.* (36) that hydroxide precipitation is not the sole mechanism for metal fixation. It should be noted that cement, Chemifix and Sealosafe samples all produced similar EXAFS and structures which demonstrated that the fixation mechanism of Zn in these three systems was the same, (ie. the addition of sodium silicate or PFA did not alter the local environment).

As far as the stabilisation of waste is concerned, the stability of this complex coating is important. The chemical bonding retains the metal pollutant in the matrix and (as can be demonstrated by dynamic leaching tests). However, the penalty of forming this stable structure is to inhibit the normal hydration of cement producing C-S-H which is responsible for strength development of cementitious system.

For metals which do not form complex precipitates with cement, this coating theory implies that they will not interfere with the normal hydration of the matrix. Microstructure analysis using SEM, XRD and MIP has shown that the hydrating matrices are not significantly affected by Hg addition. This was confirmed by the EXAFS study which demonstrated that Hg is incapable of forming a definite local environment in the various systems (OPC/PFA, OPC/silicate, OPC). This results in comparable comprehensive strength and permeability to that of a control. It also explains the relatively high leachability of Hg when compared to Zn in dynamic leaching tests (designed to assess chemical stabilisation potential).

In a PFA/OPA (Sealosafe) blended system, chemical reactions between OPC and Zn and Cd are likely to be similar to the pure cement system although the pH of the former system may be lowered by the buffering effect of the PFA. This has been confirmed by micro-analysis of SEM, XRD MIP and EXAFS. However, dynamic leaching tests on the solidified material demonstrated that the blended system immobilised more metals than the OPC system. The replacement of OPC by PFA immobilised more Zn due to the lower pH value which prevented resolubilisation of the amphoteric Sn in the alkaline environment. The amount of Ca(OH)_2 in solution was lowered - as detected by the XRD - due to reactions between Zn and Cd cations which hydroxyl ions released from the cement. This removal of Ca(OH)_2 from solution reduces the extent of an early pozzolanic reaction between lime and PFA unless an additional source of lime is present. In addition, the mechanical properties of the Zn and Cd-dosed PFA/OPC (Sealosafe) samples were also poor due to retardation of effect of these two metals of hydration and resultant modification of microstructure. The incorporation of PFA therefore, will not improve the physical properties of the solidified material.

A combination of alkaline oxide precipitation and cation exchange is thought to be responsible for the retention of Hg in the PFA/OPC system. This was confirmed in a sorption experimental study which illustrated that the PFA was able to take up Hg from solution despite the acidic environment.

Generally, a good correlation between macro (leaching, strength and permeability) and micro (SEM, XRD, MIP and EXAFS) properties has been found. Metals such as Zn and Cd which retard the hydration of cement and PFA, modify the microstructure of the matrices and produce a weak product with high permeability. Leaching tests indicate that these metals are retained in the alkaline environment of the matrices. Metals which do not retard the hydration of cement and PFA (eg. Hg) produce a microstructure environment very similar to that of a control. The mechanical properties in terms of compressive strength and permeability are also similar. However, the chemical stabilisation of these metals by cement and PFA is much smaller.

As far as the immobilisation of metal wastes is concerned, the stability of the complex coating around the cement grain is important to exploit fully the chemical fixation potential. However, promotion of this coating would seriously inhibit the normal hydration and result in a physically poor product. This has important implication for those metals relying on physical means of stabilisation.

It should be noted that the aim of the solidification/stabilisation processes is to reduce the leachability and to improve the physical properties of the solidified waste in terms of mechanical strength and permeability. Therefore, not only the reaction between the hazardous components of the waste with the stabilising materials, but the normal hydration of OPC, PFA, OPC/PFA are important. The latter affects the mechanical properties and the long term performance of the solidified material.

The mechanical properties of the solidified materials have a direct relationship with the amount of stabilising reagent added, especially a cement. Sealosafed products usually have poorer physical properties in terms of strength and permeability when compared to the Chemfix samples. This is because the contribution of PFA to strength occurs only at a later period of hydration. In addition, the use of PFA lowers the water demand of the mix and often results in the production of a layer of supernatant after all the solid had been settled. This production of supernatant can be a major source of pollution as surface runoff to a nearby watercourse. It is therefore recommended that the exposed surface area of freshly placed Sealosafe products should be kept to a minimum and sedimentation ponds or trenches should be constructed to collect runoff discharges from the land-fill area.

The problem of poor physical properties and initial surface runoff can be overcome by using a low waste/cement or waste/solid ratio. This parameter has been demonstrated to be the most important in governing settling and strength. However, as material cost, especially cement, is the most significant item in the process, the increased use of cement in the solidification process will make the process even less competitive against alternative disposal methods. The use of sodium silicate in Chemfix has been demonstrated to accelerate the initial settling and improve the initial strength. The calcium-silicate gel produced is also a powerful sorbent for water thus increasing the water demand, although the long term strength is not improved. However, experimental results of the PFA/OPC silicate system have demonstrated that sodium silicate not only increases the initial settling, but also contributes to the final strength. Therefore the selective use of sodium silicate in the PFA/OPC blended solidification process should overcome the problem of supernatant formation and promote long term strength development. However, increased dosage of sodium silicate will increase the amount of calcium-silicate gel formed. It has been shown that this gel has poor physical properties and the most damaging effect was due to shrinkage. This can result in extensive cracking in some of the solidified products and has important implications on the long term stability of the material, especially when used with highly alkaline waste.

The use of PFA has been shown to facilitate the retention of certain metals through sorption and/or chemisorption. However, due to the variability of the characteristics of PFA, a generalised conclusion is not appropriate. It is probable that almost all PFA can be used as stabilising agents at some level without significant loss of performance. But with the present paucity of knowledge of the relationship between PFA characteristics and PFA performance, it is necessary to produce a guideline for the use of these materials in the stabilisation/solidification processes.

Regarding the mechanisms of immobilisation of hazardous pollutants by the stabilising materials Lobowitz *et al.* (38) suggested that most fixatives in current practice stabilise metal contaminants through microencapsulation rather than through chemical fixation. They further suggest that a chemically 'fixed' product which needed high operating pressure and temperature was unlikely to be produced in current practice under the

normal processing conditions. They proposed that the stabilising agents (eg. cement, silicate and PFA) react with the heavy metal contaminants and cause precipitation of insoluble microscopic and macroscopic particles that are microencapsulated in the solidified cementitious matrix.

However, the definition of the term 'chemical fixation' must be clarified before any discussion on the ability of the solidification processes to chemically 'fix' any metal pollutants. One must distinguish between the chemical precipitation reaction forming an insoluble chemical compound and the crystal substitution chemical reaction in which the metal species is incorporated into hydrated matrices. The latter process has been shown in the present research to be unlikely to occur. Other research work, especially on radioactive waste, indeed showed that crystal substitution only occurred at elevated pressure and temperature (39,40) (eg. at clinkering temperature in the production of Portland cement). However, the simple precipitation and sorption reactions between metals and cement and PFA have been demonstrated to occur in the alkaline environment. The EXAFS study produced evidence that Zn was chemically bonded to the oxygen in a complex hydroxide-silicate structure.

Thus a strong chemical bonding with high dissociation energy can be realised in the simple precipitation reaction. Furthermore, it has been demonstrated that the microstructure and the physical quality of the cementitious matrix can be seriously affected by the incorporation of some heavy metals (eg. Zn, Cd). This implies that the physical means of microencapsulation proposed by Lubowitz *et al.* (38) for these metals are not valid, as leaching test studies have shown that these metals are well immobilised by the cement based stabilisation/solidification systems.

Little chemical stabilising has been shown to take place for metals like Cs with negligible chemical reaction with the stabilising agents. It has been demonstrated that the main immobilising mechanism for these metals in the cementitious matrix was the physical barrier between the waste solution and the leaching fluid. As supporting evidence, the workers reported that the most of the Cs was present in the pore fluid.

For Hg and other similar metals which form a partially insoluble compound in the alkaline environment but do not modify the microstructure of the cementitious matrix the microencapsulation theory may be appropriate to describe the immobilising mechanism. However, this is actually a combined effect of the above two mechanisms.

The above discussions illustrate that there are three levels in immobilisation of waste by the cement based stabilisation/solidification process under normal processing conditions: (i) a chemical reaction; (ii) a physical barrier between the leachate and pollutant imposed by the bulk solidified waste and (iii) a combined effect which can be described as micro-encapsulation.

Two fundamental mechanisms can thus be identified in the immobilisation of heavy metals in the cement based stabilisation/solidification process.

- (i) A chemical fixation mechanism which involves the formation of insoluble compounds between the waste components and the stabilising agent. Several chemical mechanisms take part in the reaction - involving precipitation, sorption and chemisorption. The immobilisation of Zn and Cd is mainly accounted for by this mechanism.
- (ii) A physical encapsulation in which the solidified matrices provide an impermeable barrier between the leaching fluid and the waste pollutant. This impermeable barrier relates to the physical properties of the solidified materials in terms of strength and permeability. These two properties are determined principally by the porosity of the matrices. Metals such as Hg and Cs are immobilised mainly by this mechanism.

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INTRODUCTION

In recent years there has been growing concern about the disposal of hazardous and toxic wastes (1). Methods of disposal are many and include placement in drums for burial, pooling for evaporation, storage in lined disposal sites, incineration and methods of stabilization/solidification using techniques based on cement, fly ash/lime and organic polymers such as asphalt, bitumen, ureaformaldehyde and polyester resins (2). Some of the most popular stabilisation/solidification techniques are those using a cement based technique to produce a solid monolithic mass. These techniques have been used for a number of years for heavy metal and certain inorganic wastes (3). However they are not as satisfactory for organic wastes since, unlike inorganic waste, there is little interaction between the organic material and the cementitious matrix, which results in soluble organic material and insoluble organic liquids being easily leached out by rainwater.

One possible solution to this problem would be the use of an additive that would interact with the matrix and, at the same time, adsorb the organic material, thus immobilising it. Clay minerals offer one such possibility as additives since they undergo interactions with a wide range of organic compounds and have been used for a number of years in the nuclear industry (4) for waste disposal due to their high adsorption capacity for many metals and cationic species. At the Oak Ridge Nuclear Laboratory, in the USA, the waste is blended with a dry mixture of Portland cement and a variety of clays. Some US electric utility companies employ a combination of vermiculite and cement which acts as a sponge, adsorbing liquid to produce a better final product than cement alone.

It has been known for a number of years that clays will interact with certain organic molecules, for example, they have been used to degrease wool or adsorb colour from oil (5). However, not until Ross (6) suggested a classification of clay minerals in 1928, was the modern concept of clays being composed of crystalline particles for one or more types accepted and studies of clay organic interactions gained momentum (7), with some of the earliest work being done by soil scientists investigating the interactions between soil

organic matter and clay minerals (8,9). Since the majority of organic wastes generated are aromatic in nature the objective of this paper is to review the area of clay-aromatic interactions to assess the possible use of clays as additive to a cementitious stabilisation/solidification process.

One of the first interests in clay-aromatic interactions was the study of colour reactions (10-12). These studies by Hauser (10), Kruger (11) and Weil-Malherbe (12), of interactions between aromatic amines and clays laid down some of the basic reaction mechanisms involved. Subsequently these reactions have been widely studied as a source of possible industrial and analytical applications (5).

Clay-aromatic interactions have become of importance in recent years due to the attenuation of pesticides and other toxic organics by soils and sediments (13,14) and the realisation that soils and clays can catalyse the degradation of many aromatic compounds and pesticides (15). This can result in the formation of simpler molecules such as phenols (20,28) which can lead to oligomerisation (16).

The catalytic properties of clays have also become of interest in recent years, due to the pillared clay catalysts being developed (17), which can have larger pore sizes than conventional zeolitic catalysts thus facilitating the reaction of large molecules. These catalysts are important in many high temperature, high pressure reactions. Catalysis has also been observed at ambient temperatures and pressures during studies of the reactions between non-polar molecules such as benzene (17). Since most aromatic molecules are non-polar the interaction of these compounds with clay has been studied in a variety of areas.

Clays have been extensively used as liners of hazardous waste landfill sites due to the low permeability of a packed clay bed (18). However it has been found that adsorption of organics by these liners increases the permeability by several orders of magnitude (19), and can cause the liners to shrink or expand, leading to the possibility of cracks (19,20). Iyengar et al. (21) found that chlorocarbons are absorbed mainly by hydrophobic interactions with the organic carbon fraction present.

Thus the area of clay-aromatic interactions may be broadly divided into three areas:

- (1) Reactions of non-polar molecules;
- (2) Colour reactions; and
- (3) Pesticide reactions.

The need for a safe disposal method for aromatic chemicals is compounded by the amounts and variety of waste generated. They are produced by a wide range of industries and constitute a serious potential pollution hazard. For example, polychlorinated biphenyls (PCB), a family of stable and highly toxic compounds, have a wide variety of uses in electrical capacitors, transformers, hydraulic fluids, and carbonless paper. The safe disposal of these compounds (and also soil contaminated with them) is a major problem (18). Phenols are an additional problem since they are widely used in the synthetic organic industry as a basic material (19) and are found in digested sludge from municipal treatment plants (20). Other aromatic wastes are generated by a wide variety of sources such as pharmaceutical and chemical plants, coal conversion plants, municipal treatment plants, the oil and petrochemical industries, sewage sludge and many other industrial processes.

1. Reactions of Non-polar Molecules

Since these molecules are not polar, or at least are only weakly polar, they are not expected to undergo complexation with a clay mineral as the relatively weak non-polar London and Van der Waal's forces are not strong enough to cause the displacement of interlamellar water molecules, or the separation of layers in dehydrated samples (5).

However with transition metal ion exchanged clays the possibility of complex formation with electron donating ligands exists. Indeed a wide range of copper (II) - arene complexes have been formed in the laboratory using copper (II) exchanged montmorillonite. Doner and Mortland (21) reported the first π -complex between aromatic molecules and a metal ion on the interlamellar surface of a clay mineral, using dehydrated copper (II) - Montmorillonite exposed to benzene

vapour to produce a dark red compound that was sensitive to the moisture content of the air. Mortland and Pinnavaia (22) demonstrated that there are three stages of benzene adsorption ranging from purely physically bound form through a green-yellow II-complex (type I) with partially hydrated copper (II) montmorillonite and the benzene molecule retaining its planarity and aromaticity to the original deep red (type II) complex where the molecule is extremely distorted with a subsequent reduction or loss of aromaticity. The type I and type II complexes are reversibly interconverted by controlling the degree of hydration of the complex. Since this discovery, other type I and type II complexes have been reported for a range of aromatic compounds including anisole (23), biphenyl (24) and thiophene (25) on hectorite as well as montmorillonite. It has also been found that phenol and alkyl substituted benzenes only form type I complexes (26,27).

Radical cations have been reported present with type II complexes (24,28) and to be involved in the formation of the complex. Rupert (24) also suggested that the formation of radical cations or divalent cations was the result of electron transfer from the arene to the copper (II) ion. This was later confirmed when Pinnavaia *et al.* (31) showed that the role of the transition metal ion was to simply serve as an oxidising agent to form organic radicals which then subsequently interact amongst themselves or with other organic species that are present on the interlamellar surface.

The proposed mechanism for this reaction is as follows:



where:-

Ar = aromatic molecule.

M^{n+} = transition metal cation.

It was shown (23, 29, 30) that toluene and other readily oxidised alkyl substituted benzenes did not undergo complexation to form type II complexes. This was suggested to be due to polymerisation or oligomerisation on the interlamellar surfaces (29). Mortland and

Halloran (17) subsequently confirmed this, using mass spectroscopy to show that when benzene or phenol are adsorbed on a smectite containing iron (III) or copper (II) then high molecular weight products are formed resulting from the coupling of molecules or fragments of molecules. Larson and Hufnal (31) showed that the coloured products of phenols may have molecular weights as high as 3000 and other work with several different phenols and a range of montmorillonites, exchanged with several different cations (32), showed that all the clays transformed the sorbed phenols with the greatest change being for transition metal exchanged samples. Further work with 2,6-dimethylphenol (33) showed that not only were di, tri and tetramers of the phenol formed but also quinone and quinone dimers.

In aqueous systems, adsorption of benzene and substituted benzenes is greatly reduced (34) as the interlamellar volume is occupied by the water of hydration of the exchangeable cations. The aromatics are unable to displace this water due to the relative weakness of their interactions with the cations. Thus molecules are more likely to be held by interactions with the silicate surface than with the cations. The use of organic cations, such as TMA^+ (tetramethylammonium cations) lessens this effect as the water of hydration is less strongly held creating a more hydrophobic environment between the layers and allowing greater interlamellar penetration. Thus they give improved adsorption compared with transition metal cations in these situations (34).

Work on the adsorption of phenols (19,20) and other non-polar molecules (35) by soil in aqueous systems has indicated that the organic content of the soil (35) and the water solubility of the compounds influences the extent of adsorption (19,20), presumably by increasing the extent of hydrophobic interactions between the compounds and the soil. It was found with a variety of phenols that hydrogen bonding is also an important factor and leads to greater adsorption than if hydrophobic interactions alone were responsible for adsorption (19). This type of interaction has been shown before for phenols adsorbed on clays (27,38) but these were for dehydrated samples. The strength of the interaction is greatly influenced by any substituents on the benzene ring and there is a positive correlation between the electron donating ability of the substituents (indicated by their Hammett

constants) and adsorption of substituted phenols (19,20). The introduction of an electron donating group such as -Cl increases adsorption by increasing the ability of the phenolic -OH to act as a proton acceptor. The position of the substituent is also of importance (19) and a large group in the ortho position can cause steric interference and reduce the strength of the hydrogen bonding process.

2. Colour Reactions

It has been known for a number of years that many aromatic amines convert to their coloured derivatives when they are brought into contact with clays. Hauser and Leggett (10) established some general rules from the results of studies on a wide number of amines and clays, the four principal ones being:

- (i) only aniline and related compounds give the reaction;
- (ii) the colour appears to be specific to the amine (benzidines gives blue colour, anilines green and toluidines pink or yellow);
- (iii) The colour can be lightened by drying, in some cases.

It was subsequently shown (12) that both Bronsted (acid-base interactions, with the clay acting as a proton donor) and Lewis acidity (oxidation-reduction reactions, with the clay acting as an electron acceptor), were involved. Adsorption of the organic molecules is controlled by electron transfer and by cation exchange processes occurring at both the edge and the basal surfaces of the clay crystals, the ion exchange reaction being the principal mechanism controlling adsorption (36), as shown by the pH dependence of adsorption (38), due to the pH dependence of the positive charge on the amine.

The most widely known and studied reaction in this category is the benzidine blue reaction which is used here as an example of the mechanism involved in these reactions (Fig. 1). This reaction is also shown as it is representative of the free radical oxidation catalysed by clays and soils that many aromatic compounds undergo (15). The

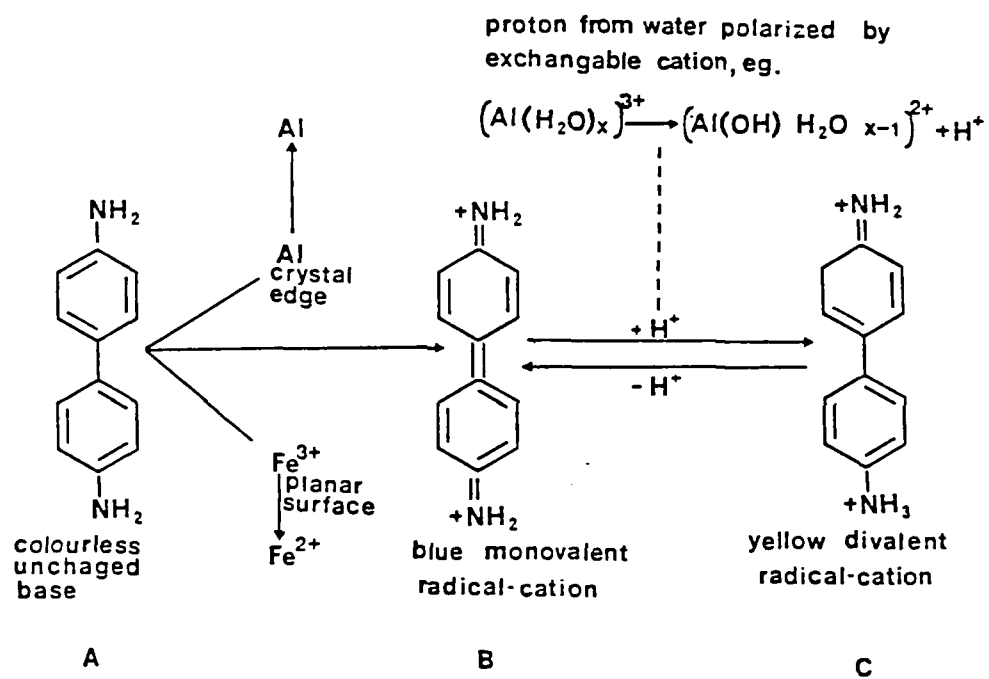


Figure 1 Diagram showing the influence of clays and pH on the transformation of benzidine into its blue and yellow cation forms (after Theng⁵).

conversion of the colourless neutral diamine (A) into its blue derivative (B) involves a transfer of an electron from the diamine to the mineral to give the blue monovalent radical cation, whose colour and stability are thought to arise from the conjugation of the unpaired $2P_z$ electron from nitrogen with the π -electron system of the aromatic ring, reinforced by resonance involving both rings. The blue species, however, only exists between pH 2.5-6, below pH 2 it can accept a proton on the lone pair of electrons of the nitrogen atom to give the yellow divalent radical cation, which has a limited number of resonance structures.

There is some uncertainty about the exact nature of the yellow species. The divalent semiquinone shown (C) has a small stabilisation resonance energy (39) and work on the diffuse reflection spectra of the system (40,41) and the failure of ESR (electron spin resonance) to show the presence of a radical led to the assignment of the colour to a quinoidal non-radical cation (39). However, for hectorite at least, it appears that the colour is due to the semiquinone radical (42) and that it is stabilised by the clay surface.

The colour of the complex is influenced by pH, below pH 2 the complex is yellow. Also the degree of hydration may affect the colour as this will also affect the acidity of the clay. Dehydration of the clay increases the Bronsted acidity of the clay which in turn produces the yellow form of the complex (43,44). The intensity of the blue colour is affected by the concentration and location of the electron sites, since the formation of the monovalent cation radical (B) involves electron transfer to the silicate surface.

It was demonstrated with a range of representative clay samples that each produced a blue colour of varying intensity when brought into contact with a saturated aqueous solution of benzidine hydrochloride. Treatment with sodium polyphosphate of kaolinite and pyrophyllite inhibited the colour reaction, whereas with montmorillonite it only reduced the intensity of the colour (44). The inhibition by polyphosphate was ascribed to its adsorption on the crystal edges. These observations led Solomon *et al.* (44,45), following earlier proposals (12,46,47), to postulate the presence of

two types of oxidising sites; firstly, at the exposed edges with exposed octahedrally bound aluminiums acting as electron acceptors; and secondly, on the planar interlayer surfaces. These sites were shown to be ferric ions occupying octahedral sites.

Later work (39,41) showed that with hectorite there is a small, fast, reaction due to structural ferric ions, as suggested by earlier work (44) but the larger and slower reaction is due to dissolved or adsorbed oxygen (42). With montmorillonite the effect of oxygen on the reaction cannot be distinguished due to the speed of the colouration from the reaction with the ferric ions (39). However, Solomon *et al.* (44) noted that the presence of oxygen increased the ease with which the oxidation occurred and ascribed this to catalytic action of oxygen at aluminium atoms on the crystal edge. The reaction with oxygen is inhibited by high pH (40,41) and McBride (42) suggested that this was the reason for the inhibition of reaction by polyphosphate rather than its adsorption on to crystal edges. Thus it seems that there is a reaction with oxygen that is possibly catalysed by edge aluminiums and is inhibited by high pH in addition to the reaction with ferric ions.

The clay surface is necessary to adsorb the benzidine molecules, to prevent the oxidation going too far or even to allow the reaction to take place (49,42). For instance as noted by Page (47) FeCl_3 will oxidise benzidine but as McBride (42) showed, it eventually gives a brown precipitate thus the clay surface must stabilise the semiquinone formed that is responsible for the blue colour. Furthermore, the addition of hydrogen peroxide to a suspension of hectorite and benzidine increases the intensity of the blue colour but on its own, without the clay, there is no visible reaction (39), showing that the clay surface plays an important catalytic role in this reaction.

It has been reported (43,46,48) that the blue colour fails to occur with kaolinite minerals and this leads to the suggestion that it be used as a method of identifying montmorillonite type minerals (46). However with modern analytical instruments clay minerals can be identified far more quickly and accurately (49), also as pointed out by Page (47) some inorganic oxidants can cause the reaction and these, if

present, would mask the clays reaction. The apparent discrepancies between the studies which report that kaolinites do undergo the reaction and those that report that they do not are probably due to variations in experimental technique and sample treatment.

The colour reactions of 2,2-diphenylpicrylhydrazil (DPPH) and some leuco dyes such as malachite green with dry montmorillonite are strongly influenced by the solvent (45). With solvents that are relatively strong electron donors such as ethanol there is no colour change as presumably the solvent is taken up in preference to the dye. The reaction with DPPH in benzene demonstrates the role that the exchangeable cation can play (apart from the direct influence on the organic molecule and the extent of interlayer expansion). When calcium montmorillonite is pretreated with polyphosphate it fails to decolour a benzene solution of DPPH but the cobalt saturated clay shows some activity possibly by acting as a "bridge" across which an electron is transferred to a ferric ion at the surface. Electron accepting species can also form complexes with (reduced) montmorillonites as is shown by the reaction of TCNE (tetracyanoethylene) to give a red tone radical-cation (45).

In the petroleum industry it has been found that Asphaltenes and resins which are structurally similar to many organic dyes are rapidly and nearly irreversibly adsorbed on to montmorillonites (50,51) by a reaction that appears to be similar to that for benzidine blue (50). There is also a very clear solvent effect and in solvents such as nitrobenzene with high dielectric constants the molecules become ionized and there is increased adsorption due to ion exchange reactions. The exchange cation also causes variation in adsorption in the order $Mg > Ca > Na > K$ except with nitrobenzene where the promotion of a K^+ -nitrobenzene complex increases adsorption so that the order becomes $K > Mg > Na > Ca$. Adsorption appears to be mainly on the external surfaces of the clay particle.

3. Pesticide Reactions

In the last forty years there has been a vast increase in the usage of synthetic organic pesticides. With the use of these chemicals has come the awareness of the importance of the interactions bet-

ween the compounds and soil constituents, among them the clay minerals. The term pesticide is used here to denote a wide range of synthetic compounds used to control weeds and insects. Pesticides may be grouped into three broad categories according to their predominant charge characteristics; cationic, anionic and non-polar. The interaction of each of these classes with clay minerals (and other soil constituents) has been discussed by Baily and White (13). These characteristics affect the interaction with the clay mineral and thus the pH of the system and the pKa of the compound become important in these reactions. Cationic pesticides are adsorbed by clays through an ion-exchange process, replacing the cations initially present at the mineral surface. With the remaining two classes of compounds pH can affect adsorption quite markedly, in the anionic species, at low pH, acidic functional groups may accept protons to give the uncharged form of the molecule, at other pH's where this does not occur the negative charge on the molecule causes it to be repelled from the negative silicate surface, non-polar species may also become protonated, in acidic media, acting as cations. However at the normal pH generally found in soils they are predominantly in their molecular form and thus their adsorption is controlled by ion-dipole interactions, such as those already mentioned for benzene.

The most widely used non-polar pesticides are the substituted s-triazines, however, due to the presence of three nitrogen atoms in the ring these compounds display very little aromatic character and hence their adsorption is controlled by the substituent groups at the 2, 4 and 6 positions rather than the heterocyclic ring (5). Thus these compounds are not especially relevant to this article. However, similar results for substituted compounds with greater aromaticity (50,51), such as the substituted phenyl ureas, which show a linear relationship between the logarithm of the partition coefficient and the Hammett constants (of the ring substituents).

An early attempt was made to elucidate the mechanisms underlying the clay pesticide reactions using a range of organic herbicides taken up by montmorillonite, illite and kaolinite from aqueous systems (52). This was shown as a function of pH and electrolyte concentration and demonstrated that where a compound exists in its uncharged form (due to pH) - as is the case of non-polar pesticides

under normal soil conditions - adsorption must take place by replacing the water molecules from the clay surface. Thus the bonding is not strong, montmorillonite shows a greater uptake than illite or kaolinite due to its larger available surface. The ability of a clay to take up the pesticide is dependent on the latter's ability to penetrate the interlamellar space and this will be facilitated if the layers are more expanded - as in sodium montmorillonite in an aqueous system or if the pesticide is protonated to give the cationic form, which can be brought about by the use of a hydrogen exchanged clay (the latter effect is stronger) (53).

Work by Bailey *et al.* (53) showed that for non-polar compounds in a given chemical family adsorption is controlled by, and is a function of, the solubility of the pesticide in water, whereas between families the basicity (pKa) is important. However, as might be expected, transition metal, organic or polyvalent cations give rise to clay-organic interactions, either directly or through a water bridge (54,55). From the work by Mortland and co-workers seen earlier and others (55,56), this mechanism could well be the most important factor in the adsorption of non-polar compounds.

The work by Bailey *et al.* (53) also demonstrated negative adsorption for a wide range of anionic pesticides using sodium montmorillonite, although the use of hydrogen montmorillonite produced a positive adsorption for some of the compounds. This suggests that the primary mechanism of anion adsorption is due to proton association and adsorption of the molecular species by Van der Waals type adsorption. In addition, hydrogen bonding between any carbonyl groups present and the silicate surface cannot be ignored. This work supports the work of Frissel and Bolt (52) which demonstrated that 2,4-D and 2,4,5-T (2,4-dichloro- and 2,4,5-trichloro-phenoxy acetic acid) have negative adsorption in the range pH 4-10, where the anionic species would be present, while below about pH 3 there is positive adsorption where the molecular form would predominate. The negative adsorption of these two herbicides has been confirmed (56,57) with montmorillonite, illite and kaolinite.

The most widely used and studied cationic pesticides are diquat and paraquat and these will be used as examples to show the general

reaction that this type of pesticides are involved in. These compounds are taken up from aqueous solutions by montmorillonite and kaolinite in amounts approaching the cation exchange capacities of the minerals (58). This infers an ion exchange reaction with the bipyridinium ions replacing the cations originally present on the surface. However, ultra-violet and infrared spectroscopy later showed that there is also a charge transfer involved between the quarternary pyridinium cation and the anionic silicate surface (59,60). Both compounds are strongly adsorbed with interlayer penetration on montmorillonite (58) but only surface adsorption on kaolinite (i.e. on external bases and edge surfaces) and therefore are more strongly bound to the montmorillonite.

As would be expected for these charged species the charge characteristics of the silicate surface are important as shown by the dissimilarities in their adsorption by montmorillonite and vermiculite (60-62). The more diffuse smaller charge on sodium montmorillonite allows the cations to assume a planar configuration between the layers, whereas the more localised higher charge density of sodium vermiculite presents this due to the more tightly bound water and smaller interlayer distances (61), leading to exothermic adsorption for the montmorillonite but endothermic for the vermiculite.

Additionally it has been shown (64) that minerals with higher surface charge preferred diquat whilst those of lower charge preferred paraquat. It was suggested that the charge separation on the herbicides was important (64-66) and that the pesticide with a charge which approached that of the clay charge sites the closest would be preferentially adsorbed. Later, calculations of the charge distributions of diquat and paraquat showed that they were both very similar and diffuse leading to the rejection of this earlier suggestion (62).

DISCUSSION AND CONCLUSIONS

The chemical differences between the different classes of compounds encountered in hazardous waste disposal means that uneven adsorption of organics would occur for a single clay system, thus each waste would have to be treated with the appropriate clay system to give optimum adsorption of all the organics. These clay systems would

probably need to contain more than one clay, each of which would adsorb a particular compound, or group of compounds, better than the rest.

One of the most important factors to be considered in a clay for this use would be the exchangeable cation, as shown by Doner and Mortland (21) and McBride *et al.* (34), as this can profoundly affect the adsorption of a compound. Whilst sodium and calcium exchanged montmorillonites will adsorb a variety of organic molecules (67) they will not significantly adsorb aromatic molecules such as benzene (21). The use of transition metal exchange cations overcomes this problem with the formation of donor-acceptor complexes, although this effect is somewhat negated in aqueous systems (34) due to the strongly bound water molecules. This also can be overcome by the use of organic cations that bind the water less strongly and create a more hydrophobic environment between the layers. One problem with this may be finding cations that will hold the layers far enough apart to allow intercalation of large molecules, such as chlorobenzenes, without them buckling and taking up interlayer space (68) thus decreasing the surface area of the clay.

The charge properties of the clays can also have an influence on the extent of reaction (21). The origin of the charge in a clay mineral i.e. whether it is due to substitution in the octahedral or the tetrahedral layers - effects the charge density and this can influence both polar (64) and non-polar (21) molecules. For instance Swoboda and Kunze (70) showed that clays with tetrahedral charges tend to react with weaker bases than those with predominantly octahedral charges. The overall charge on a layer is controlled by the extent of substitution and this can be controlled by effecting the migration of lithium ions into the holes in the octahedral layers (69), causing changes in the charge distribution, surface area and swelling properties of the clays.

As has been shown aromatics are not necessarily non-polar compounds and side chains can have a considerable influence on the nature of them. Obviously, anionic species will present a problem due to the negative charge on the silicate surface leading to repulsion. However as shown by Frissel and Bolt (52) with anionic

pesticides this can be countered by adjusting pH or by using a hydrogen exchanged clay as demonstrated by Bailey *et al.* (53). The use of clays with a low surface charge (reduced charge clays) may also prove to be useful for this type of compound.

The cationic species may prove easier to adsorb as shown by the uptake of diquat and paraquat by kaolinite and montmorillonite to almost the equivalent of the exchange capacity of the minerals (58). This is controlled by pH which can control the charge on the molecule and also the surface charge characteristics of the clay. The surface charge of the clay is important in the adsorption of cationic species (64).

The non-polar molecules are by far the largest group of compounds that need considering. They have a weak interaction with most clays due to the relatively weak van der Waals type interactions that they undergo. However, the use of transition metal cations causes complexation in fully or partially dehydrated systems (21). This effect is weakened in aqueous systems due to the water of hydration (34). However, the use of organic cations overcomes this and allows adsorption to take place, although as previously mentioned large molecules, such as chlorobenzenes, may have trouble intercalating into a tetramethylammonium exchanged clay, for example, due to the interlayer spacings (66).

As well as undergoing adsorption reactions with aromatic molecules, clays also catalyse reactions as evidenced by the benzidine blue reaction (44) and the oligomerisation of phenols (33). These reactions are free radical oxidation reactions and Dragun and Helling (15) have proposed guidelines based on four groups of aromatic compound grouped according to substituents on the ring and the lower water solubility limit. They propose that compounds found within these groups may undergo free radical oxidation. Such compounds include benzene, phenol and many others but compounds such as PCBs will not be so oxidised. Thus the use of clays to adsorb organics may modify a compound and accelerate its degradation.

Most wastes will not be single component systems and therefore each system will have to be treated differently according to the che-

minerals present and there may be some need for a pretreatment such as acidification or the mixing of different types of waste to create the optimum system. This problem is compounded by variations in the waste stream that would require alterations to the additive formulation. Also the optimum clay adsorbent for each class of compounds will differ and therefore the composition of a waste will need to be taken into consideration and it may be necessary to add more than one type of clay. Multicomponent systems also present problems in that there will be competing reactions going on at the same time which will reduce adsorption compared to a single component system.

There are several advantages to be gained with the proposed technique. At best it would mean that organic and inorganic wastes can be treated at the same time and as one waste, at worst kept separate and treated at the same site. There would be less use of the ponding of organic wastes with the risk of leakage and it would be cheaper than storage in drums and other methods such as incineration and detoxification, which can also produce their own handling/disposal problems. Thus it would present an easier, cheaper and safer method of disposal than those currently used for a wide range of wastes.

Thus when considering this approach to the problem of hazardous organic waste disposal it can be seen that there are many factors to be assessed before a waste can be successfully treated. However, the use of these minerals as an additive to a cementitious system would seem to offer a promising method of dealing with organic waste material and might cause an accelerated degradation of the waste. Research is now being undertaken to evaluate their use in conjunction with cement-based stabilisation/solidification systems as a method of treating hazardous organic waste.

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